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Tailoring dicobalt Pacman complexes of Schiff-base calixpyrroles towards dioxygen reduction catalysis**

Elham Askarizadeh,[1,2] Sahar Bani Yaghoob,[1,2] Davar M. Boghaei,[2] Alexandra M. Z. Slawin[3] and Jason B. Love[1,*]

[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[2]Department of Chemistry, Sharif University of Technology, P.O. Box 11155-3516, Tehran, Iran.

[3]EaStCHEM School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, UK.

[*]Corresponding author; e-mail: jason.love@ed.ac.uk; fax: +44 (0)131 6504743;

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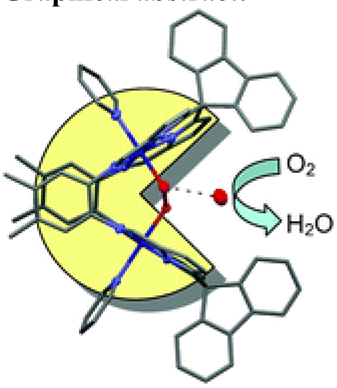
Supporting information:
[†]Electronic Supplementary Information (ESI) available: full experimental, crystallographic and catalytic data and Figures S1 to S5. CCDC 749304 and 749305 See http://dx.doi.org/10.1039/B923189G

Graphical abstract:



Keywords:
porphyrin-corrole dyads; O bond activation; hangman porphyrins; fuel-cells; oxygen; reactivity; water, O-2; architectures; cobalt(III)

Abstract

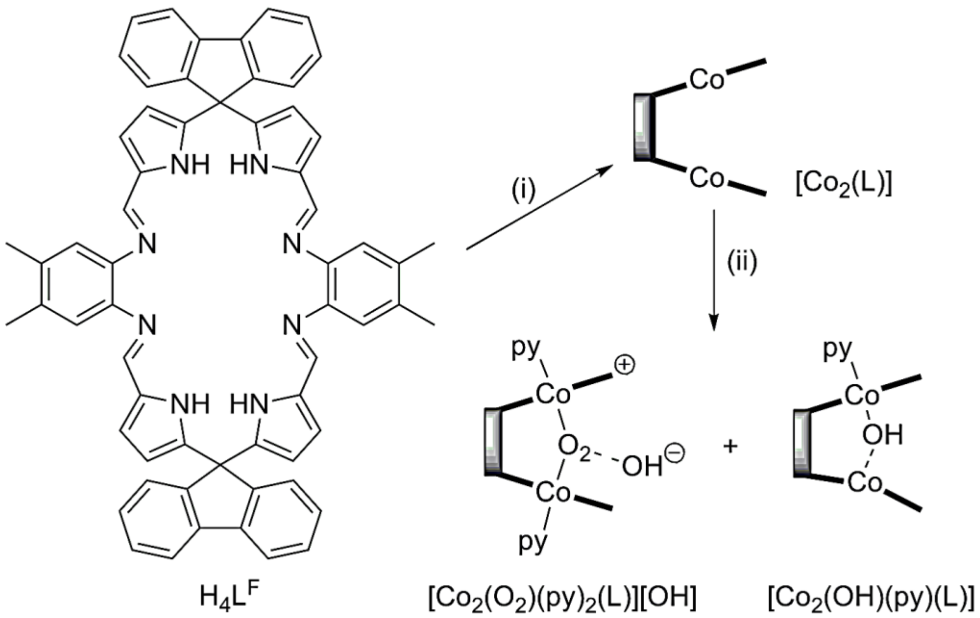
By modifying the mouth of a macrocyclic dicobalt Pacman complex, it is possible to both isolate new bridging-superoxo and hydroxyl complexes and to tune the reactivity of this system towards catalytic four-electron reduction of dioxygen to water.

Introduction

The reduction of dioxygen is a chemical reaction intrinsic to fuel cells and aerobic organisms and relies on transition metal-based compounds or enzymes to manage the multiple proton and electron inventory during catalysis and ensure the efficient and selective generation of water. Much effort has gone into elucidating a fundamental understanding of this proton-coupled, multi-electron redox reaction,[1] in particular to help develop new, base-metal catalysts that are more robust and economical than the Pt-based materials currently used in polymer electrolyte membrane fuel cells.[2] In this context, molecular systems such as cofacial or Pacman dicobalt diporphyrins and corroles have proved very effective as catalysts for dioxygen reduction and the spectroscopic, structural, and theoretical analysis of these systems has provided much detail of the mechanism, in particular the identification of the superoxo complex $[Co_2(\mu\text{-}O_2)(\text{diporph})]^+$ as a key director of selectivity.[3-6]

As an alternative to these porphyrinic complexes that are typically difficult and time-consuming to synthesise, we found that the dicobalt Pacman complex $Co_2(L)$, in which the Schiff-base calixpyrrole ligand L has methyl *meso*-substituents, reacts with air to form a 90:10 mixture of the peroxo complex $Co_2(\mu\text{-}O_2)(py)_2(L)$ and the superoxo cation $Co_2(\mu\text{-}O_2)(py)_2(L)^+$; the former peroxo complex was characterised structurally and displayed a zigzag bonding mode of the O_2^{2-} unit between the two metals.[7] This mixture of compounds acted as a catalyst for the selective four-electron reduction of oxygen to water, albeit slowly and with decomposition, and we proposed that this poor activity profile was due to a combination of the formation of a stable hydroxyl-bridged cation $Co_2(\mu\text{-}OH)(L)^+$ coupled with difficulty in accessing the superoxo cation, the entry point into the catalytic cycle.[8] We reasoned that the use of sterically-hindering, aryl *meso*-groups such as fluorenyl in L^F would both obviate the formation of μ-OH bridged compounds and change subtly the electronic nature of these compounds, features that could promote better catalytic activity. We present here the significance of this ligand modification on the oxygen chemistry of its dicobalt complexes.

The $Co^{II}Co^{II}$ complex $Co_2(L^F)$ was prepared as described previously,[9] and reacted with air in the presence of pyridine to form a mixture of two new complexes, the $Co^{III}Co^{III}$ superoxo cation $\{Co_2(\mu\text{-}O_2)(py)_2(L^F)\}\{OH\}$ and the mixed valence $Co^{II}Co^{III}$ hydroxyl-bridged complex $Co_2(\mu\text{-}OH)(py)(L^F)$ that are related *formally* by O_2 loss (Scheme 1).



Scheme 1. Synthesis of dicobalt compounds of the macrocycle H_4L^F. Reagents and conditions: (i) 2 $[Co(THF)\{N(SiMe_3)_2\}_2]$, THF; (ii) Air, py, THF.

This reaction was monitored by ^1H NMR and EPR spectroscopies.† In the ^1H NMR spectrum (SI, Fig. S1), addition of pyridine to a $CDCl_3$ solution of $Co_2(L^F)$ causes the well-resolved, but paramagnetically-shifted signals of $Co_2(L^F)$ to disappear and, on exposure of this mixture to air, new resonances to appear between +40 and -70 ppm that are consistent with the asymmetric environment of the new $Co^{II}Co^{III}$ paramagnetic complex $Co_2(\mu\text{-}OH)(py)(L^F)$. This formulation is supported further by addition of [D_5]-pyridine to the mixture which results in exchange of only one molecule of pyridine (SI, Fig. S1) and also by X-ray crystallography (see below). Significantly, there is no evidence of any diamagnetic peroxo complex $Co_2(\mu\text{-}O_2)(py)_2(L^F)$ in any of these NMR spectra, which contrasts to that seen by us in the oxygenation reactions of $Co_2(L)$.[7] In the X-band EPR spectrum in frozen $CHCl_3$ (SI, Fig. S2), the broad, featureless resonance for $Co_2(L^F)$ at *g* 2.214 is replaced by a less intense (24% by integration), S = ½ signal centred at *g* 2.016 on exposure to air which is best assigned to the superoxo cation $Co_2(O_2)(L^F)^+$; no signal is seen in fluid solution. Simulation of this resonance in rhombic symmetry suggests that the oxygen radical is bound primarily to *one* Co centre, with g_x 1.991, A_x 11.5 G, g_y 2.015, A_y 14.0 G, and g_z 2.068, A_z 21.5 G, which contrasts to the 15-line EPR spectra seen normally for superoxo cobalt cofacial diporphyrin complexes and also for $Co_2(O_2)(L)^+$ in which the O_2^- is bound symmetrically between the two Co^{III} centres. This suggests that the O_2^- is bound either in an asymmetric manner within the cleft or that it coordinates to a single Co outside the cleft.

The superoxo complex $\{Co_2(\mu\text{-}O_2)(py)_2(L^F)\}\{OH\}$ was isolated as an analytically-pure material from hot toluene solution.‡ The frozen solution X-band EPR spectrum of this isolated material is identical to that seen in the *in-situ* experiments, and the IR spectrum displays a broad absorption at 3398 cm^{-1} which supports the presence of hydrogen-bonded hydroxide; dark red prisms were grown from toluene from which the X-ray crystal structure was determined (Figure 1).†

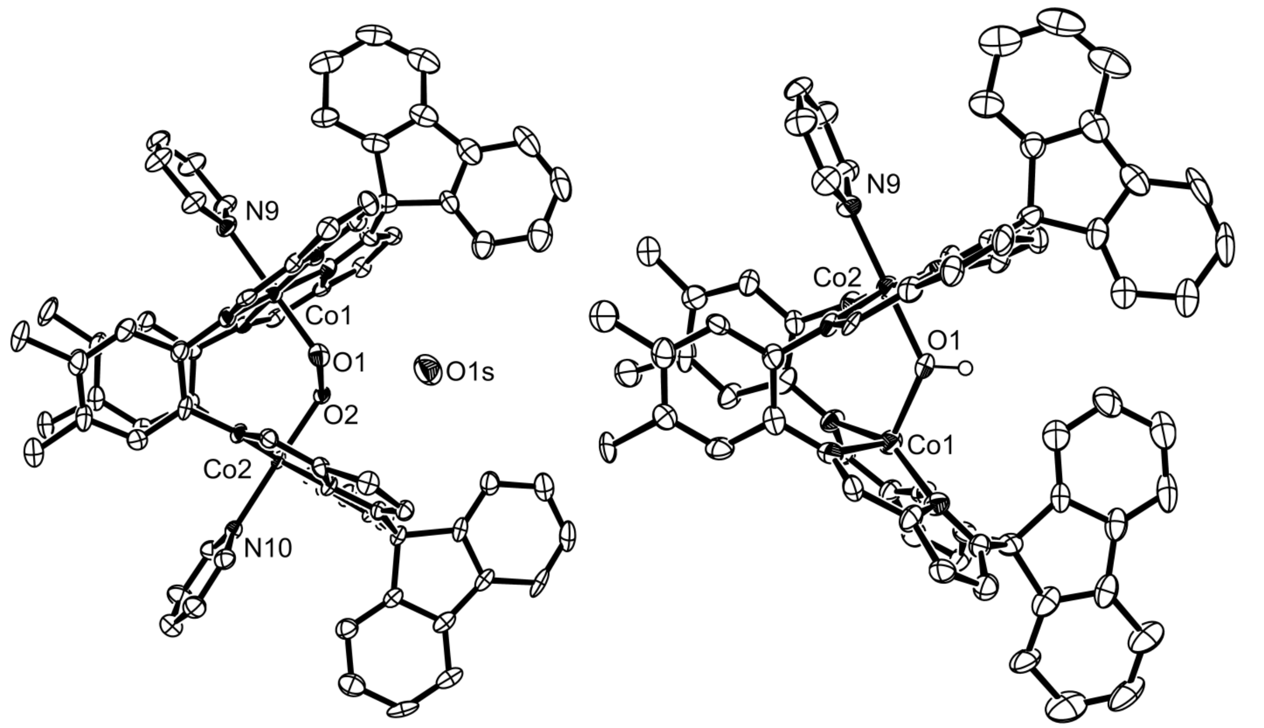


Figure 1. The solid state structures of $\{Co_2(\mu\text{-}O_2)(py)_2(L^F)\}\{OH\}$ (left) and $[Co_2(\mu\text{-}OH)(py)(L^F)]$ (right). For clarity, all hydrogen atoms, except on the bridging hydroxyl oxygen and solvent of crystallisation have been omitted (displacement ellipsoids are drawn at 50 % probability).

In the solid state, the O_2 is bound asymmetrically within the Co_2 cleft (Co1-O1 1.907(4), Co2-O2 1.942(3) Å) with an O1-O2 bond distance of 1.389(4) Å and a Co1···Co2 separation of 4.15 Å. Although the O-O distance is similar to that seen by us in the solid state structure of the *peroxo* complex $Co_2(\mu\text{-}O_2)(py)_2(L)$ (1.361(3) Å), DFT calculations carried out by us on this latter peroxo compound and the singly-oxidised superoxo complex $Co_2(O_2)(py)_2(L)^+$ showed the O-O bond distances to be identical (difference 0.001 Å) and so a poor measure of the electronic structure.[8] The slightly elongated O-O bond in this case is likely a consequence of the different ligand environment and the strong hydrogen-bonding interaction seen between O1 and the hydroxide O1s (O1•••O1s 2.801 Å). Analysis of a space-filling model of $\{Co_2(\mu\text{-}O_2)(py)_2(L^F)\}\{OH\}$ (SI, Fig. S3) shows that O1s is nestled tightly in a cleft formed between the two fluorenyl substituents and the bridging O_2 and that the fluorenyl substituents also display π-stacking interactions with a molecule of pyridine that binds in a cleft adjacent to the hydroxyl group. Intermolecular hydrogen-bonding interactions between metal-coordinated O_2 and a donor such as H_2O or ROH are observed frequently in Ti, V and Mo O_2 complexes in which the O_2 is side-on bound (mean $O_2\cdots O$ shortest contact 2.97 Å)[10] but to a much lesser extent in binuclear $Co_2(\mu\text{-}O_2)$ compounds (4 examples, range 3.187-3.653 Å; mean $O_2\cdots O$ shortest contact 3.35 Å).[11] This interaction may suggest that the bound-O_2^- in $\{Co_2(\mu\text{-}O_2)(py)_2(L^F)\}\{OH\}$ is more basic than in previous examples, a feature desirable in oxygen reduction catalysis in which protonation of the superoxo cation is a key mechanistic step that leads to O_2 scission and water production.[5] The ^1H NMR spectrum of analytically-pure, crystalline $\{Co_2(\mu\text{-}O_2)(py)_2(L^F)\}\{OH\}$ in $CDCl_3$ displays only resonances attributable to $Co_2(\mu\text{-}OH)(py)(L^F)$ and implies that the O_2 ligand is substituted readily by the OH^- ligand.

The hydroxyl-bridged compound $Co_2(\mu\text{-}OH)(py)(L^F)$ is less soluble than the superoxo complex $\{Co_2(\mu\text{-}O_2)(py)_2(L^F)\}\{OH\}$, and a few poorly-diffracting red prisms were isolated from $CDCl_3$ and the X-ray crystal structure determined (Figure 1).† As with the superoxo cation, a wedged, Pacman structure is seen, in this case with a hydroxyl-group bound asymmetrically between the two cobalt cations (Co1-O1 1 .987(5), Co2-O1 1.916(5) Å) which are separated by 3.53 Å. The distorted octahedral coordination sphere of Co2 is completed by a molecule of pyridine, while Co1 adopts a square pyramidal geometry, moving 0.59 Å out of the N_4-donor plane into the molecular cleft (*c.f.*-0.07 Å for Co2). Hydrogen-bonding contacts between the OH^- group and both the fluorenyl group and a molecule of $CHCl_3$ are also seen (SI, Fig. S4) and may provide additional stability to the solid state structure. These geometric features, along with the longer Co-N(pyrrole) and Co-N(imine) bond distances seen for Co1 compared to Co2 and the absence of a counter ion, shows that $Co_2(\mu\text{-}OH)(py)(L^F)$ is a rare example of a mixed valence $Co^{II}Co^{III}$ hydroxide in which the hydroxyl ligand bridges the two metals asymmetrically.

Preliminary evaluation of the catalytic activity of oxygenated $Co_2(L^F)$ towards oxygen reduction was carried out using a modification of Fukuzumi and Guilard's method in which ferrocene derivatives (Fc) act as one-electron reductants in air-saturated PhCN in the presence of acid.[12] For $Co_2(L^F)$, the best data were obtained using $(C_5H_4Me)_2Fe^+$ with 9.6×10^{-5} M of catalyst and 0.4 M of CF_3CO_2H (background production of ferrocenium was subtracted),[4] and resulted in the generation of $(C_5H_4Me)_2Fe^+$ that became asymptotic at 6.2 mM concentration after 100 s (Fig. 2); this concentration of $(C_5H_4Me)_2Fe^+$ equates primarily to a four-electron reduction process, *i.e.* the formation of H_2O in preference to H_2O_2 ($[(C_5H_4Me)_2Fe^+]$ expected 6.8×10^{-3} M with $[O_2] = 1.73 \times 10^{-3}$ M).†

Similar data were obtained using the less reducing Cp_2Fe as the electron source although in this case asymptotic behaviour was only seen after 600 s (Fig 2, dashed lines). The use of lower concentrations of catalyst results in a decrease in total $[Fc^+]$, which may suggest that the catalytically-active species has a moderate turnover. Even so, the catalytic activity of $Co_2(L^F)$ is enhanced significantly when compared to $Co_2(L)$ under the same conditions (Fig. 2, 0.024 mM, Cp_2Fe^+) and suggests that the ligand modification moving from L to L^F has generated a much more robust catalyst. The rate of formation of $(C_5H_4Me)_2Fe^+$ obeys pseudo-first order kinetics, and k_{obs}, obtained from the pseudo-first order plot varies linearly with catalyst concentration with the second order rate constant $k_{cat} = 6.1 \times 10^2\ M^{-1}s^{-1}$ (SI, Fig. S5). This value of k_{cat} is ca.

600 times less than that of the best cofacial diporphyrin catalyst for four electron O_2 reduction, Co_2(DPX), where $k_{cat} = 3.6 \times 10^5\ M^{-1}s^{-1}$ (DPX has a xanthene single pillar between the two porphyrins).[12]

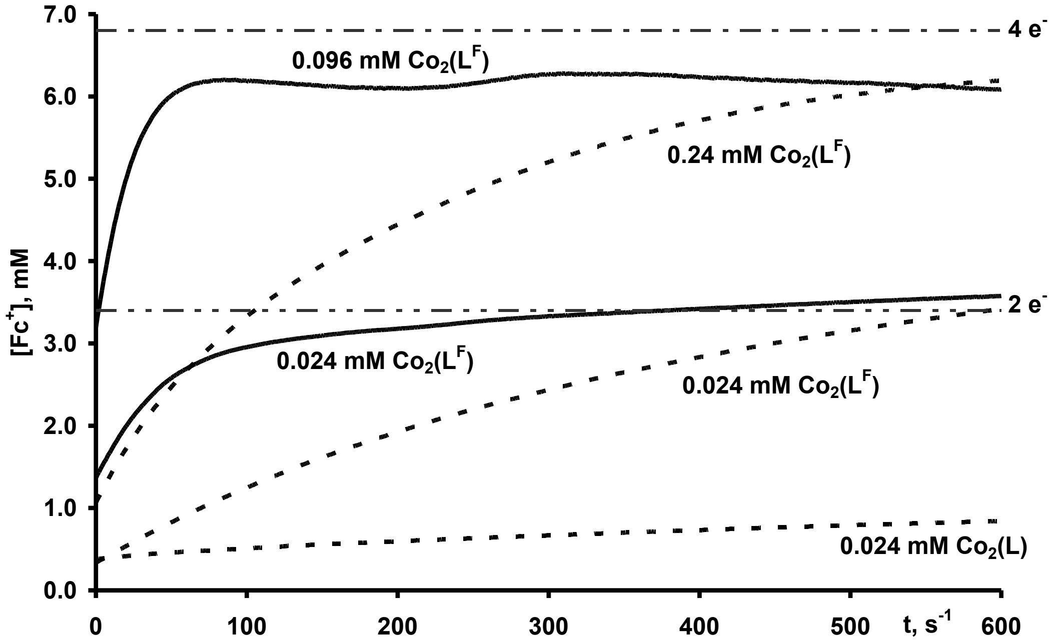


Figure 2. Time profiles for the formation of Fc^+ (solid lines $(C_5H_4Me)_2Fe^+$, dashed lines Cp_2Fe^+) monitored by UV-vis spectrophotometry in the electron transfer oxidation of Fc by O_2 (1.73×10^{-3} M) catalysed by $Co_2(L^F)$ or $Co_2(L)$ in the presence of 0.4 M CF_3CO_2H in PhCN at 298 K.

It is clear that the presence of the fluorenyl *meso*-substituents in $Co_2(L^F)$ modifies significantly its reactions with O_2, forming the two new compounds $\{Co_2(\mu\text{-}O_2)(py)_2(L^F)\}\{OH\}$ and $Co_2(OH)(py)(L^F)$, and transforming a compound that is a relatively poor catalyst for four-electron dioxygen reduction into one that is considerably more effective. Detailed mechanistic assessments of the dioxygen chemistry of related cobalt cofacial diporphyrin complexes have shown that the entry point into the catalytic cycle for dioxygen reduction is the mixed valence cation $Co_2(\text{diporph})^+$ that reacts reversibly with O_2 to form the superoxo cation $Co_2(O_2)(\text{diporph})^+$; this latter compound is the key director for the reduction reaction.[1, 4-6] In contrast, the oxidation of $Co_2(L^F)$ occurs spontaneously on exposure to air to form the mixed valence compound $Co_2(OH)(py)(L^F)$ which can react with O_2 to form the key superoxo complex $\{Co_2(\mu\text{-}O_2)(py)_2(L^F)\}\{OH\}$, so forming a mixture that are effective oxygen reduction catalysts.

Notes and references

‡Syntheses: $\{Co_2(O_2)(py)_2(L^F)\}\{OH\}$ – Solid $Co_2(L^F)$ (0.10 g) was dissolved in air-saturated THF (20 mL), causing an immediate red to dark brown colour change. Pyridine (0.04 mL) was added, and after 3 h, hexane (100 mL) which caused the products to precipitate. The precipitate was collected on a frit and extracted into hot toluene (60 °C, 60 mL), filtered, and reduced in volume. The crude product was precipitated by the addition of hexane and isolated as a brown powder (0.064 g, 54 %). Red brown crystals of $\{Co_2(O_2)(py)_2(L^F)\}\{OH\}$.py.2PhMe were grown by hexane diffusion into a toluene/pyridine mixture.

Found: C, 70.47; H, 4.50; N, 11.46. $C_{72}H_{55}N_{10}O_3Co_2$ requires: C, 70.53; H, 4.52; N, 11.42 % ^{1}H NMR ($CDCl_3$, 360 MHz, 298 K): δ_H 36.7 (s, 1H), 32.5 (s, 2H), 31.3 (s, 2H), 30.5 (s, 2H), 21.6 (s, 6H), 20.6 (s, 2H), 17.5 (s, 1H), 16.8 (s, 2H), 14.5 (s, 1H), 14.4 (s, 1H), 13.7 (s, 1H), 11.9 (s, 1H), 10.0 (s, 1H), 5.5 (s, 1H), 4.8 (s, 1H), 4.4 (s, 2H), 2.1 (s, 1H), 0.9 (s, 1H), 0.8 (s, 2H), -5.0 (s, 1H), -5.8 (s, 1H), -16.4 (s, 6H), -22.3 (s, 1H), -30.4 (s, 1H), -63.1 (s, 2H).; IR (KBr, nujol): ν 3398, 2927, 2853, 1559, 1463, 1377, 1054, 739, 446 cm^{-1}; UV-Vis (THF): λ_{max} 332 nm (ln ε 11.12), 257 (11.29), 221 (11.4); ESI-MS (+ve ion): *m/z* 1052 (M^++ H - OH, 100 %), 1036 (M^++H - OH – O, 52), 1019 (M^++H - OH – 2O, 12).

Red crystals of $Co_2(OH)(py)(L^F)$.4$CDCl_3$ were grown by the slow evaporation of a sample of $\{Co_2(O_2)(py)_2(L^F)\}\{OH\}$ in $CDCl_3$.

Crystal data $\{Co_2(\mu\text{-}O_2)(py)_2(L^F)\}\{OH\}$ $C_{72}H_{55}N_{10}O_3Co_2(C_5H_5N)(C_7H_8)_2$, M 1489.49, a 14.4714(4), b 14.8327(4), c 18.8570(6) Å, α 78.571(2), β 75.865(2), γ 71.571(2)°, T 150(2) K, triclinic, P-1, Z 2, 43676 reflections 15079 independent , R(int)0.084, $R[F^2 > 2\sigma(F^2)]$ 0.100, CCDC 749304; $Co_2(\mu\text{-}OH)(py)(L^F)$ $C_{67}H_{49}N_9OCo_2(CHCl_3)_4$, M 1592.49, a 20.627(2), b 22.087(3), c 30.628(4) Å, $\alpha = \beta = \gamma = 90$°, T 150(2) K, orthorhombic, *Pbca*, Z 8, 85490 reflections 12745 independent , R(int)0.29, $R[F^2 > 2\sigma(F^2)]$ 0.098, CCDC 749305.

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